

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
30 June 2005 (30.06.2005)

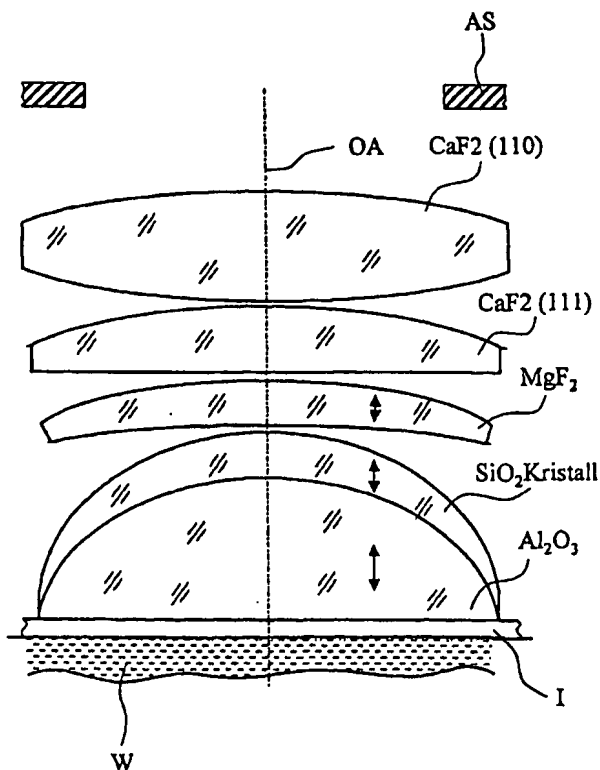
PCT

(10) International Publication Number  
WO 2005/059645 A2

- (51) International Patent Classification<sup>7</sup>: G03F (72) Inventor; and  
(75) Inventor/Applicant (for US only): SCHUSTER, Karl-  
(21) International Application Number: PCT/EP2004/014100 Helnz [DE/DE]; Rechbergstrasse 24, 89551 Königsbronn  
(DE).  
(22) International Filing Date: 10 December 2004 (10.12.2004) (74) Agent: MÜLLER-RISSMANN, Werner; c/o Carl Zeiss  
AG, Patentabteilung, 73446 Oberkochen (DE).  
(25) Filing Language: English (81) Designated States (unless otherwise indicated, for every  
kind of national protection available): AE, AG, AL, AM,  
(26) Publication Language: English AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN,  
CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI,  
GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE,  
KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD,  
MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG,  
PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM,  
TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM,  
ZW.  
(30) Priority Data: 60/530,623 19 December 2003 (19.12.2003) US  
60/568,006 4 May 2004 (04.05.2004) US  
(71) Applicant (for all designated States except US): CARL  
ZEISS SMT AG [DE/DE]; Carl Zeiss Str. 22, 73447  
Oberkochen (DE). (84) Designated States (unless otherwise indicated, for every  
kind of regional protection available): ARIPO (BW, GH,

[Continued on next page]

(54) Title: MICROLITHOGRAPHY PROJECTION OBJECTIVE WITH CRYSTAL ELEMENTS



(57) Abstract: A microlithography projection objective is proposed with optical elements, i.e. lenses or planar-parallel plates (used as end-closure plates) of crystalline magnesium fluoride, quartz, lanthanum fluoride, sapphire and Alpha-aluminium oxide. Suitable crystallographic orientations, crystal 10 combinations, and polarizations of the light are described. Suitable applications are for immersion lithography or near-field lithography in the DUV and VLN range, using the highest numerical aperture values.

WO 2005/059645 A2



GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Declarations under Rule 4.17:**

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, NA,

SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)

- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii)) for all designations
- of inventorship (Rule 4.17(iv)) for US only

**Published:**

- without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guide to the Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

Microlithography Projection Objective with Crystal Elements

5 The invention relates to a microlithography projection objective with crystal elements, namely such made from materials showing birefringence and other than cubic crystal structure.

10 These are of relevance mainly as some of them show refractive indices well above those of quartz glass or calcium fluoride, what is a substantial need for immersion lithography with image side numerical apertures beyond 1.0 up to about 2 or more.

15 From publications such as

Bruce W. Smith et al. Optical Microlithography XVII  
Proc. SPIE 5377 (2004), p 273 -284;

20 Bruce W. Smith et al. Optical Microlithography XVI,  
Proc. SPIE 5040 (2003), p 679 -689;

John H. Burnett et al. "High Index Materials for 193 nm and 157 nm Immersion lithography"

25 Int'l Symp. on Immersion & 157 nm Lithography, Vancouver  
8/2/04 (NIST/ Corning Tropel)

and patent applications such as  
WO2004/019 128 A2,

30 or, commonly owned with this application:

US 6,717,722 B,

US Ser. No. 10/734,623 filed 15 Dec. 2003,

US Ser. No. 60/530,623 filed 19 Dec. 2003,

US Ser. No. 60/530,978 filed 22 Dec. 2003,

35 US Ser. No. 60/544,967 filed 13 Feb. 2004,

US Ser. No. 60/568,006 filed 04 May 2004,

US Ser. No. 60/592,208 filed 29 July 2004,

US Ser. No. 60/591,775 filed 27 July 2004,

US Ser. No. 60/612,823 filed 24 Sept 2004,

40 DE 10 2004 051 730.4 filed 22 Oct. 2004

some information about this art can be gathered.

45 Of these, e. g. WO 2004/019 128 A2, US 10/734,623, US 60/592,208, US 60/591,775 and US 60/612,823 show objective designs which can be optimized by and combined with the use of materials and teachings according to this application.

50 Suitable immersion liquids are inter alia described in US 60/568,006 or DE 10 2004 051 730.4.

All cited documents are incorporated into this application by reference in their entirety.

- 5 Their citation in no way constitutes any declaration on their relevance for this application, and the list certainly is incomplete and many more publications relate to this art.

□

- For end-closure plates or for the last-positioned lens  
10 element in immersion objectives or near-field objectives there is a need for optical materials of the highest possible index of refraction. At the same time, the materials need to be transparent, homogeneous, radiation-resistant, as well as mechanically and chemically robust. There is a material  
15 which meets all of these conditions except for optical isotropy. The material is sapphire or, in chemical terms,  $\text{Al}_2\text{O}_3$ . Others are  $\text{MgF}_2$  or  $\text{LaF}_3$  and other uniaxial crystals.

- In an absolutely telecentric light path and with completely  
20 tangential polarization it is possible to achieve complete isotropy of the light-transmitting properties by using the measures proposed by the present invention.

- The claims together with this specification describe  
25 solutions to these problems and advantageous varieties.

- Figures 1 to 8 and 10 to 13 are sketches that illustrate the principles of arrangements, or parts thereof, according to the invention.

- 30 Figure 9 shows wavelength-dependent variation of  $n_o$  and  $n_e$  for some materials from an article.

- In the illustrated arrangements, for example in Figure 2, the  
35 sum  $(n_o - n_e)\text{Al}_2\text{O}_3 + (n_o - n_e)\text{SiO}_2$  equals zero for a maximum-aperture

ray  $B_{\max}$  with an incident angle of  $70^\circ$  ( $n_o$  refractive index of ordinary ray,  $n_e$  refractive index of extraordinary ray).

The following symbols are used in the drawings:

5

AS = aperture stop / system aperture

P = protector plate / protective element

I = immersion fluid, immersion

W = wafer, or the object to be exposed in the image plane

10 OA = optical axis

L = lens

$B_{\max}$  = ray of maximum aperture

With tangential polarization of the light rays there is only  
15 one component, namely the p-component, and as a consequence,  
there is no phase shift between p- and s-components as long  
as the optical crystal axis of the crystal is oriented in  
exact parallel alignment with the optical axis of the  
objective. However, these conditions are met only  
20 approximately in practical cases. As a means to achieve  
perfect isotropy in the effect that a plate of this kind has  
on light rays, it is proposed according to the present  
invention that the plate be made of two parts. The proposed  
combination consists of an  $Al_2O_3$  sapphire plate  $P_1$  of optically  
25 negative character and an  $SiO_2$  crystal plate  $P_2$  of optically  
positive character, as illustrated in Figures 1 to 3. The  
magnitude of the birefringence changes individually with the  
wavelength. The plate thicknesses are therefore selected  
dependent on the wavelength, so that a birefringence of the  
30  $Al_2O_3$  plate is compensated by the complementary birefringence  
of the  $SiO_2$  plate. This cannot be achieved completely,  
because the indices of refraction are different for the two  
materials, so that a compromise is necessary for different  
incident light angles. However, an exact compensation can be

achieved in particular for the highest apertures which are relevant in immersion lithography applications, e.g., for dipole illumination.

5 In addition to a planar plate, the invention can also be used in a lens element. Since  $\text{Al}_2\text{O}_3$  sapphire offers one of the highest known indices of refraction for the wavelengths of 157 nm and 193 nm, it is a preferred material to use for the element in the last position of the objective. Elements of  
10 crystalline  $\text{SiO}_2$  are placed (in direction of light propagation) before the  $\text{Al}_2\text{O}_3$  element.

Figure 4 represents a sketch to illustrate the principle, wherein the symbol QG stands for quartz glass, QK for quartz  
15 crystal, S for sapphire (which is at the same time a lens L in the sense of Figure 1).

It also makes sense to use arrangements of elements that are joined together by wringing. The fact that the absolute  
20 amount of birefringence is larger in crystalline quartz is of practical significance because less of the  $\text{SiO}_2$  crystal is needed for compensation. Also, crystalline  $\text{SiO}_2$  has the smaller index of refraction and its use at the image-oriented end of a high-aperture immersion objective is therefore less  
25 advantageous.

An arrangement that is suitable for example for a wavelength of 193 nm is shown in Figure 5. The spaces between the lenses, particularly in the area near the image plane where  
30 there are large ray angles relative to the optical axis, can be filled by high-refractive fluids FL1 of the same kind that are also used as an immersion medium. A double arrow in the lenses indicates the orientation of the optical axis of the birefringence that is inherent in the materials.

It is clear that the effective index of refraction in the crystals  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  is subject to a continuous angle-dependent variation, but with tangentially polarized light  
5 there is initially no phase shift between an s-polarized and a p-polarized component. The variation of the refractive index is taken into account in the design.

Figure 6 illustrates an example of an objective for an  
10 operating wavelength of 157 nm with  $\text{CaF}_2$  lenses of different crystallographic orientation, for example 111 and 110, for the compensation of intrinsic birefringence with a pair of optically uniaxial crystal lenses that is compensated in accordance with the invention. With immersion I or the near-  
15 field lithography technique, the objective can be coupled to the object to be exposed, for example a wafer W, with the largest possible numerical aperture.

Because of the high light-gathering power (etendue), it is  
20 preferred to make the compensation. This is the best way to master the problem of extended fields outside of the telecentric light path without the split between s-polarization and p-polarization. Of course, with a skewed incident radiation in birefringent crystals, the  $n_o$ -components  
25 run outside the plane of incidence. However, with the different character of  $\text{SiO}_2$  crystal and  $\text{Al}_2\text{O}_3$  sapphire, it is possible to take specifically targeted countermeasures.

The term "negative optical character" means that the  
30 refractive index  $n_o$  of the ordinary ray is larger than the refractive index  $n_e$  of the extraordinary ray.

The term "positive optical character" means that the refractive index  $n_o$  of the ordinary ray is smaller than the refractive index  $n_e$  of the extraordinary ray.

5 The scope of the invention includes: the compensation as described; the use of  $Al_2O_3$ , sapphire and  $SiO_2$  crystal in lithography optics; the placement of the elements between the aperture stop or a conjugate location of the aperture stop and the image plane of a projection objective, with special  
10 preference for placing these elements in the bottom one-third of the distance between the aperture stop and the image plane; the use of the aforementioned materials for protector plates for immersion or near-field arrangements, either by themselves without compensation, or with compensation; the  
15 use at high angles of incidence  $>60^\circ$ , with special preference  $>70^\circ$ ; including in these applications the compensation at the highest numerical aperture values NA (above 1.3 to 1.6) on the image side; also including the use of tangentially polarized light; and further including the use in immersion  
20 objectives with a refractive index of more than 1.8 in the last optical element, with special preference for more than 2.0; and also the use at an operating wavelength of 157 nm in conjunction with the crystals  $CaF_2$ ,  $SiO_2$ ,  $Al_2O_3$ , sapphire - in respectively different combined arrangements.

25 Similar to silicon dioxide, magnesium fluoride in crystalline form has an optically positive character. The advantage of  $MgF_2$  lies in its high UV transmittance, particularly at 157 nm. Its drawback is the low coefficient of refraction,  
30 for example at a wavelength of 193.304 nm, with values of  $n_o = 1.427460$  and  $n_e = 1.441069$ .

The compensation of birefringence in a high-aperture end-closure part of a microlithographic projection objective .



- requires the availability of suitable degrees of freedom. If the birefringence were of exactly equal magnitude and had the same form in  $\text{Al}_2\text{O}_3$  as in quartz crystal, an exact solution that provides compensation for all angles would exist at least for planar-parallel plates, i.e., one would only need to use two plates of equal thickness. If lenses are used instead of plates, the possible phase differences occurring as a result of refraction and birefringence become larger and there is an increased risk that this will affect the image quality. On the other hand, with lenses one has the possibility to use a targeted variation of the radii as a further degree of freedom in addition to the thickness, as a parameter for compensation.
- Based on these considerations, a further material is proposed for an additional fine correction, namely  $\text{MgF}_2$  crystal. In view of its low index of refraction, it is placed preferably in a position before the more strongly refractive elements of quartz crystal and sapphire. It should be noted in this context that the uniaxial birefringent crystals  $\text{Al}_2\text{O}_3$ , sapphire,  $\text{SiO}_2$ ,  $\text{MgF}_2$  are compensated in an entirely different manner than the  $\text{CaF}_2$ ,  $\text{SrF}_2$ , and  $\text{BaF}_2$  crystals and the like which are a priori isotropic (at least in the visible range).
- The refractive index of the successive elements, for example at the 157 nm wavelength in the example of Figure 7, is continuously increased towards the wafer (image plane), namely up to a level of more than 2.0.
- The optical path lengths for s- and p-polarization are largely equalized for the broadest possible range of angles through the simultaneous use of three crystalline materials  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , and  $\text{MgF}_2$ . It should be noted that the harmful contributions for skewed rays increase the farther one moves

these elements away from the wafer, i.e., from the image plane. This also provides the special possibility of a compensation based on where a lens of each of the respective materials is positioned. The optical path length should to  
5 the greatest extent possible meet the condition

$$(n_o - n_e)Al_2O_3 \cdot d_1 + (n_o - n_e)SiO_2 \cdot d_2 + (n_o - n_e)MgF_2 \cdot d_3 = 0,$$

wherein  $n_o$  represents the refractive index for the ordinary ray,  $n_e$  represents the refractive index for the extraordinary ray, and  $d_1$ ,  $d_2$ ,  $d_3$  represent the respective path lengths  
10 inside the crystals. It should be the aim (and it is possible) to meet the condition particularly well in the aperture angle range from 65° to 72°.

The scope of the invention likewise includes a lithography  
15 objective in a projection system, where the effect of birefringence of uniaxial crystal materials in end-closure plates or lenses on the image side of the objective is completely corrected for angles in the range from 65° to 72° (measured geometrically from the optical axis).

20

Instead of using  $Al_2O_3$ , sapphire for the compensation or as a provider for the primary refractive power in this end range, one could also use the uniaxial crystal material  $LaF_3$  as a further possible lens material. Like  $Al_2O_3$ , it has a negative  
25 optical character and the birefringence values likewise resemble those of  $Al_2O_3$ . In comparison to sapphire,  $LaF_3$  has the advantage that the commercially available crystals, which are made in a completely different manufacturing process, currently meet higher standards of optical quality.  $LaF_3$  is  
30 water-insoluble, but it does not come up to the levels of hardness and UV transmittance of  $Al_2O_3$ , sapphire.

Figure 8 schematically illustrates an example for an operating wavelength of 193 nm where  $LaF_3$  is used for the last

lens on the image side, in this case with a protector plate P  
of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. In this case, too, the alternative to an  
arrangement with an immersion fluid is an optical near field  
where the distance between the protector plate P and the  
5 wafer is shorter than the operating wavelength.

With this plate P of Al<sub>2</sub>O<sub>3</sub>, it is very important to pay  
attention to the fact that the  $\alpha$ -modification of the crystal  
represents the advantageous choice. The  $\gamma$ -modification of  
10 Al<sub>2</sub>O<sub>3</sub> is hygroscopic and should not be used.

Table 1:

Refractive indices of the uniaxial crystals

wavelength	MgF <sub>2</sub>	
	ordinary	extraordinary
248.338 nm	1.403248	1.416080
193.304 nm	1.427460	1.441069
157.629 nm	1.466666	1.481281

wavelength	SiO <sub>2</sub>	
	ordinary	extraordinary
248.338 nm	1.601568	1.612689
193.304 nm	1.660455	1.673963

Difference between indices  $\Delta n = n_o - n_e$ 

157.629 nm	Al <sub>2</sub> O <sub>3</sub>	0.012973
	MgF <sub>2</sub>	0.014243

- 5 The birefringence values were measured by the interference method and are more reliable than measuring the indices  $n_o$  and  $n_e$  by means of prisms and taking the differences. In regard to this topic, reference is also made to an article in Applied Optics, March 1969, Volume 8 No. 3, p. 673, where the
- 10 wavelength-dependent variation of  $n_o$  and  $n_e$  is discussed.

Figure 9 is copied from Fig. 3 of the aforementioned reference.

- 15 Further according to the invention, uniaxial crystals are compensated as follows:

- Lenses LPP of positive refractive power and positive optical character are compensated by lenses LPN of positive
- 20 refractive power with negative character (Fig. 10). In

addition, lenses of positive refractive power can also be compensated with lenses of negative refractive power with the same character, as shown in the example of Figure 11 - with positive character in the lenses LPP, LNP (negative

5 refractive power), possibly supplemented by a lens LPN.

Figure 12 shows an arrangement where lenses LPN, LNN, LPP follow each other, with LNN being a lens of negative refractive power and negative optical character.

- 10 As a further example, Figure 13 shows the four last lenses on the image side of a microlithography projection objective with the materials according to the invention as the significant mass (material) of the lenses, which may be coated with layers for antireflection, anticorrosion or the
- 15 like (as in the other embodiments discussed), i.e., MgF<sub>2</sub> / SiO<sub>2</sub>, crystal / optional fluid lens / LaF<sub>3</sub> / Al<sub>2</sub>O<sub>3</sub>, sapphire, and with appropriate compensation of imaging errors due to birefringence effects of the lens materials.

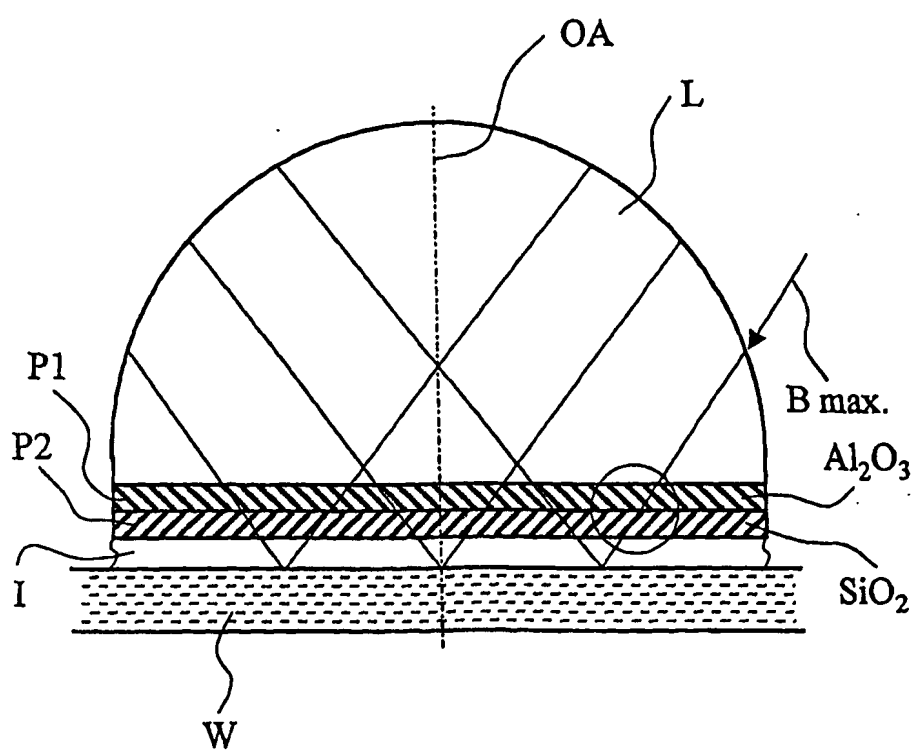
## Patent Claims:

1. Microlithography projection objective with at least one  
lens of quartz crystal and with at least one lens of  
5 sapphire crystal.
2. Microlithography projection objective with at least two  
transmittent optical elements, in particular lenses (L)  
or planar-parallel plates (P) consisting of crystals that  
10 are uniaxial with regard to birefringence, wherein at  
least two of said optical elements consist of different  
crystal materials.
3. Microlithography projection objective according to claim  
15 1 or claim 2, characterized in that an axis of  
birefringence of a first optical element and an axis of  
birefringence of a second optical element each run  
parallel to the optical axis of the geometrical light ray  
path inside the projection objective.  
20
4. Microlithography projection objective according to at  
least one of the preceding claims, characterized in that  
said lenses (L) or optical elements (P) are arranged on  
the image side of a pupil or system aperture (AS) that is  
25 nearest to the image plane.
5. Microlithography projection objective according to at  
least one of the preceding claims, characterized in that  
said lenses (L) or optical elements (P) are among the  
30 three optical elements that lie closest to the image  
plane (W).
6. Microlithography projection objective according to at  
least one of the preceding claims, characterized in that

the numerical aperture on the image side is larger than 1.6 and with special preference larger than 1.8.

7. Microlithography projection system with a  
5 microlithography projection objective according to at least one of the claims 1 to 6.
8. Microlithography projection system according to claim 7,  
10 characterized in that polarized light passes through said crystalline lenses or crystalline optical elements.
9. Microlithography projection system according to claim 8,  
characterized in that the light is tangentially polarized.
- 15 10. Microlithography projection system according to claim 8,  
characterized in that the light is linearly polarized.
11. End-closure plate of a microlithography projection  
20 objective substantially made of  $\alpha\text{-Al}_2\text{O}_3$ .
12. Use of an  $\text{LaF}_3$  lens or  $\text{LaF}_3$  planar-parallel plate in a  
microlithography projection objective.
- 25 13. Microlithography projection objective with at least two  
optical elements from the group that comprises lenses and  
planar-parallel plates substantially consisting of a  
material from the group that comprises crystals of  $\text{MgF}_2$ ,  
30  $\text{SiO}_2$ ,  $\text{LaF}_3$ , sapphire,  $\alpha\text{-Al}_2\text{O}_3$ .
14. Microlithography projection objective according to claim  
13, characterized by the presence of two or three  
different materials selected from said group of crystals.

1/9

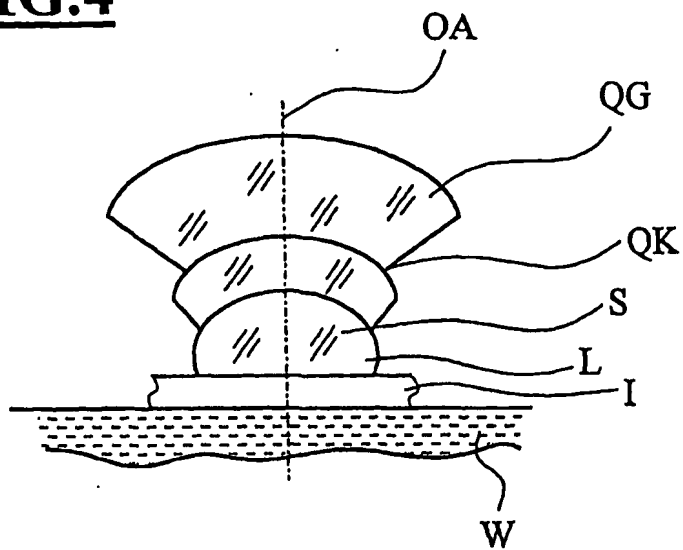
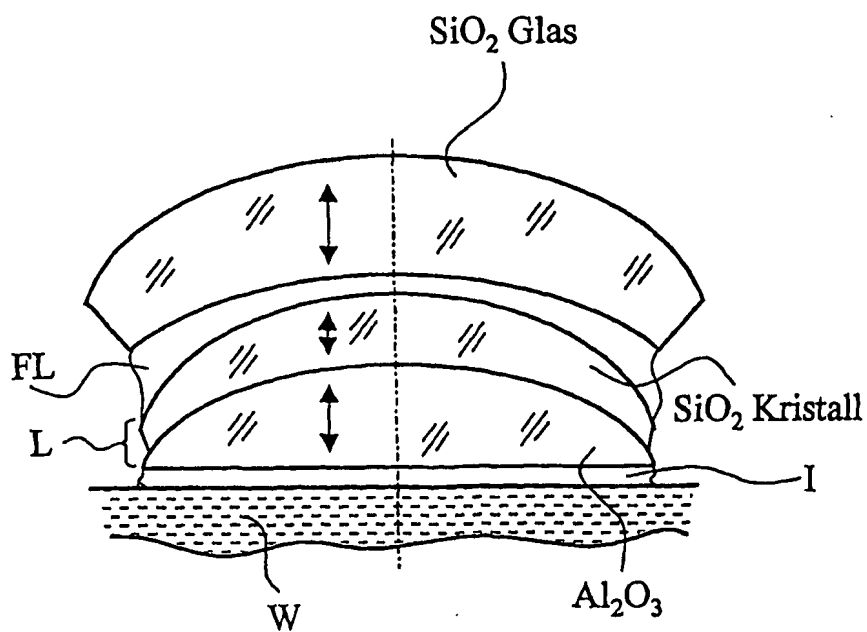
**FIG.1**



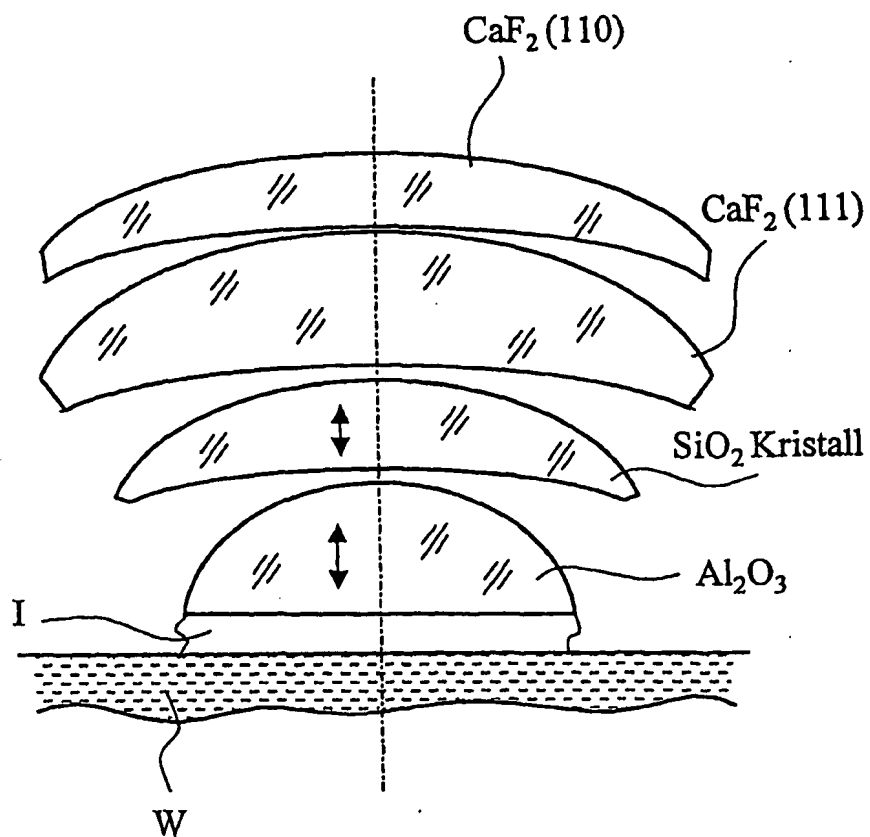
**WO 2005/059645**

**PCT/EP2004/014100**

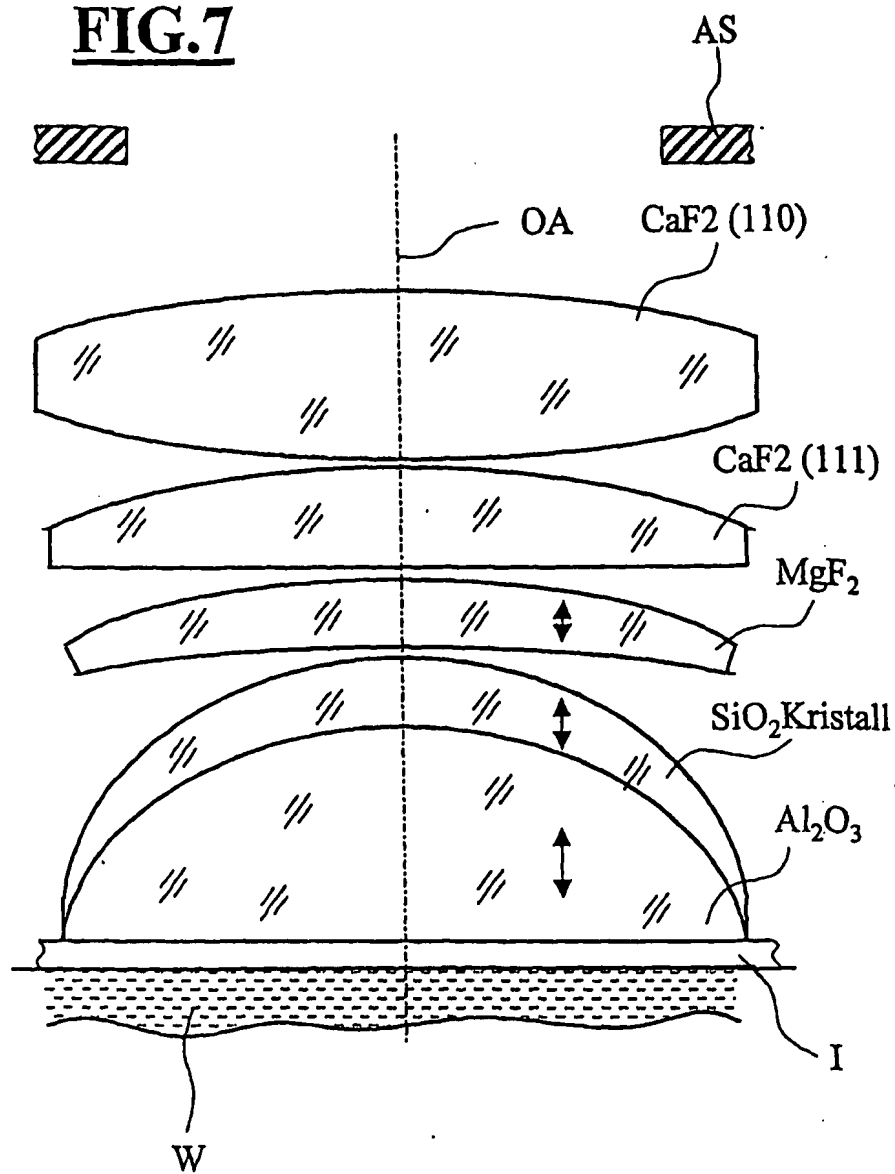
3/9

**FIG.4****FIG.5**

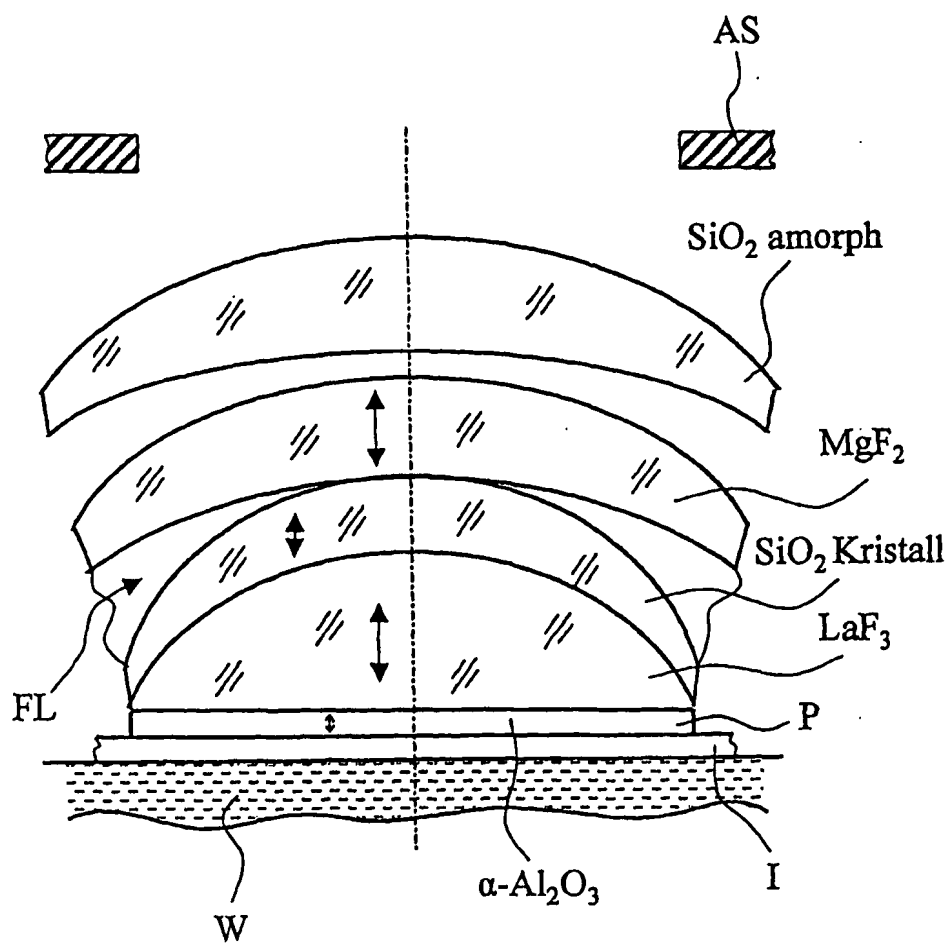
4/9

**FIG.6**

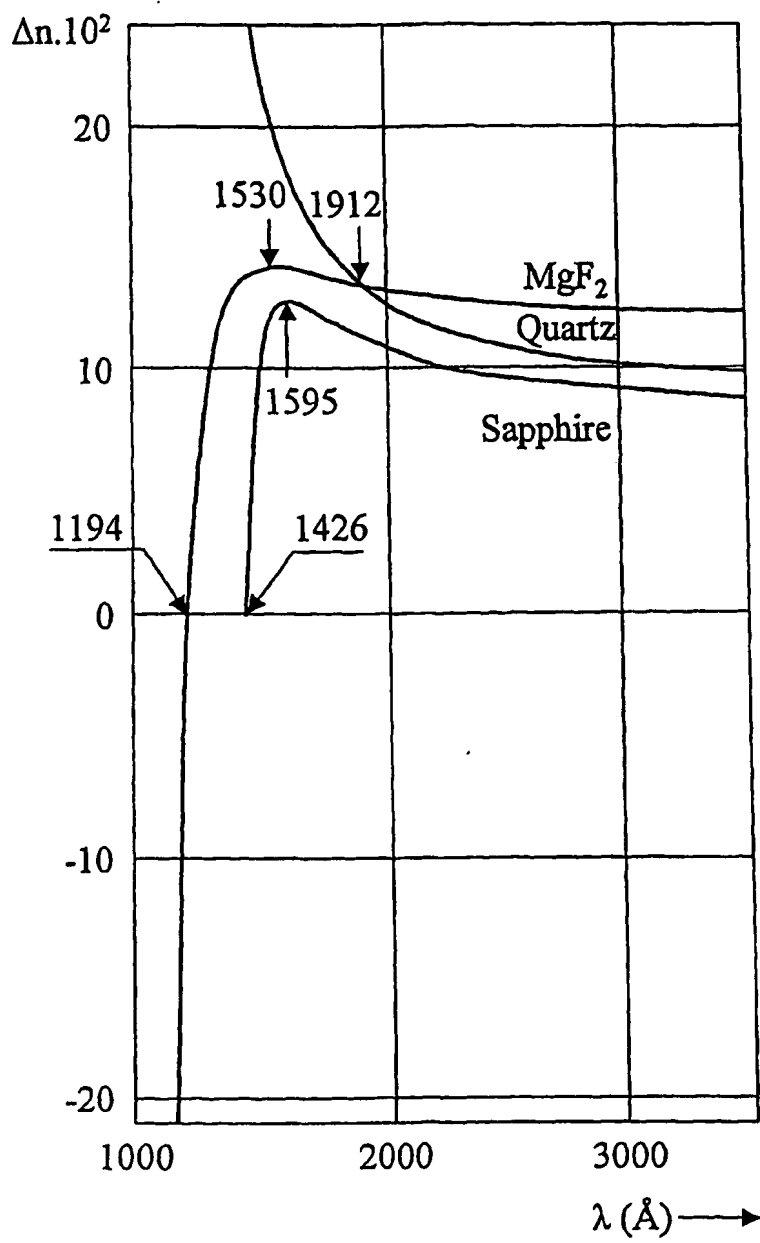
5/9

**FIG.7**

6/9

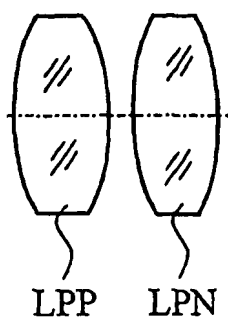
**FIG.8**

7/9

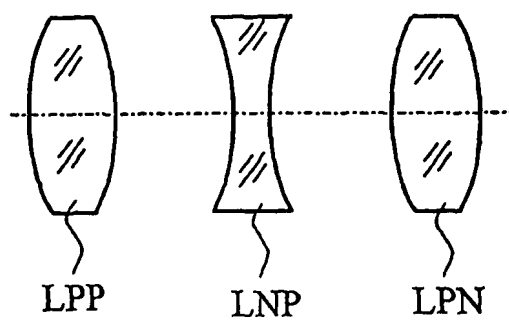
**FIG.9**

8/9

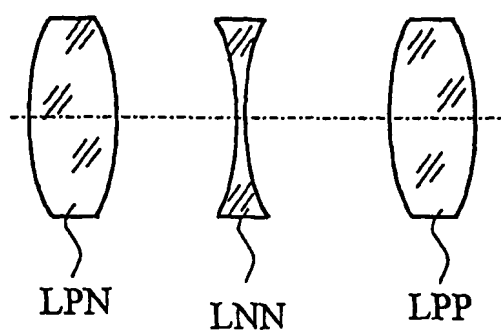
**FIG.10**



**FIG.11**



9/9

**FIG.12****FIG.13**